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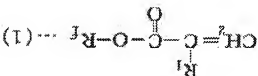
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(54) FLUORINE-CONTAINING, SURFACE-TREATMENT AGENT

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a fluorine-containing, surface-treatment agent capable of imparting sufficient stain resistance and anti-fogging properties to a substrate to be treated. SOLUTION: The fluorine-containing, surface-treatment agent comprises a copolymer containing, in an amount within 1-70 mass%, a fluorine-containing vinyl monomer (A) bearing a fluoroalkyl group represented by formula (1) (wherein R1 is hydrogen or a 1-3C alkyl group; and Rf is an alkyl group containing fluorine atoms in the range of 2 to 31).



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CLAIMS

[Claim(s)]

[Claim 1] A fluoride content finishing agent, wherein a fluoride system vinyl monomer (A) which has a fluoro alkyl group expressed with a following formula (1) contains a copolymer contained in the range of 1 - 70 mass %.

[Formula 1]

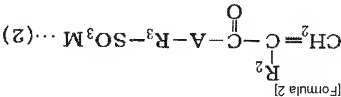


(R1 in a formula is hydrogen or an alkyl group of the carbon numbers 1-3, and Rf is an alkyl group which contains a fluorine atom in 2-31.)

[Claim 2] In the finishing agent according to claim 1, the above-mentioned copolymer, Besides the above-

mentioned fluoride system vinyl monomer (A), tertiary amine or the 4th class ammonium content vinyl monomer (B), And a finishing agent, wherein it is a copolymer of both sexes amphiphilicity which contains an anionic vinyl monomer (C) as an essential ingredient and ratios of ** (B) and (C) are 10 - 90-mol% in B/(B+C).

[Claim 3] In the finishing agent according to claim 1, the above-mentioned copolymer, A finishing agent which is a copolymer of hydrophilic oil repellency which contains a sulfone group content hydrophilic nature vinyl monomer (D) expressed with a following formula (2) other than the above-mentioned fluoride system vinyl monomer (A) as an essential ingredient, and is characterized by containing ** (D) in this copolymer in the range of 20 - 95 mass %.



(R2 in a formula is hydrogen or an alkyl group of the carbon numbers 1-3, A is O or NH, R3 is the straight chain shape, the branched state alkylene group, or alkenylene group of the carbon numbers 1-15, and M is hydrogen, alkali metal salt, or an ammonium derivative.)

[Claim 4] A finishing agent which is independent to a processed substrate which has a hard surface in the finishing agent according to any one of claims 1 to 3, or is characterized by spraying applying with a detergent, or making this processed substrate immersed, and giving fog resistance and antifouling property to this processed substrate.

[Claim 5] A finishing agent making a processed substrate which has a soft surface immersed with independence

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or a detergent in the processed substrate.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the fluoride content finishing agent used for a surface modifier etc. It can use for refining of soft surfaces, such as hard surfaces and hair, such as stainless steel and a plastic, and textiles, especially, and is related with the fluoride content finishing agent which gives antifoaming and an antifog function to those processed surfaces.

[0002]

[Description of the Prior Art] Generally the art of processing soft surfaces, such as a hard surface and hair, such as stainless steel, glass, and various plastics, and textiles, is developed, and antifoaming property and fog resistance are given to a processed substrate by this processing. About such a finishing agent, various proposals are made from the former. For example, the finishing agent containing the amphoteric polymer compound obtained by copolymerization of a cationic vinyl monomer and an anionic vinyl monomer for plastics is indicated by JP, 62-260895, A. This finishing agent has a point which should be improved to the adsorptivity to the object face of a surface treatment, etc. The 4th class ammonium content vinyl monomer, a carboxyl group containing vinyl monomer, and an acrylamide (meta) system vinyl monomer are used as an essential ingredient, and the polymers copolymer with the structure to which this was made to carry out copolymerization of the other vinyl monomers is indicated by JP, 53-149292, A. It is not a finishing agent [aiming at the fog resistance of a processed substrate, or antifoaming property] aiming at this copolymer being used for a paper reinforcing agent or a polymer coagulant, and giving paper durability enhancement and a condensation function. The emulsion composition of the fluoride synthetic resin which makes two or more sorts of fluorine system vinyl monomers come to polymerize is indicated by JP, 2-191654, A. Although this constituent is proposed as a cheap surface-active agent, improvement is still expected from the performance, handling, etc.

[0003] The detergent composition for tableware containing the 2 yuan copolymer of an anionic vinyl monomer and a cationic vinyl monomer is indicated by JP, 1-55320, B. Surface reforming treatment is not expected in such a detergent composition for tableware. The thing using the high molecular compound which has the fluorine atom which combined JP, 3-234870, A with the carbon atom of the main chain, for example, a tetrafluoroethylene vinyl ether copolymer, is known. However, since dilution use is carried out by organic solvents, such as toluene and xylene, when there is a process of processing a low fluoride content water and oil repellent agent further and a low fluoride content water and oil repellent agent is used after processing **** by a high fluoride water and oil repellent agent in this case, a work environment top problem is seen. JP, 9-59041, A is made to distribute a silicon precursor in carrier fluid, and the finishing agent which gives fog resistance to a processed substrate side via photocatalyst is indicated, this used the reaction — half— it is a lasting surface treatment method. The finishing

agent processed with the fluorene polymer which processes metal salt more than divalent for the textiles which are processed substrates, next contains in JP,7-34384,A the hydrophilic functional group in which this metal and coordination are possible is indicated. Since the treating operation of this finishing agent is impossible in once, its work is complicated.

[0004]Conventionally, the finishing agent using a fluorene system copolymer is also developed. For example, although JP,2-132101,A, JP,2-147601,A, etc. other than above-mentioned JP,2-191654,A and JP,7-34384,A are mentioned, these do not dissolve in a drainage system solvent. Therefore, it is considered as the emulsion. The ingredient for forming an emulsion in addition to polymers is needed, and this has the problem that a product combination presentation is restricted from the point of securing product stability. A finishing agent has many things which contact by anticipated use and which are [moisture] easy too much and can take a processing agent easily with water etc., and is expected the modifier which has durable antifouling and antifog function. [0005]It does not adhere easily and various finishing agents which give hydrophilic oil repellency as a substrate which can be dropped easily are also proposed in recent years. usually, as for surface wettability, work of adhesion wettability is defined by the formula of Young (young people) from the formula of Dupre-Good ("----- - good). What what generally shows oil repellency shows water repellence as surface character, and shows hydrophilic nature from these formulas shows lipophilic property. On the other hand, after after desiccation shows water repellence and the surface immerses it in water, the polymers (film-top mechanism) from which the surface changes to hydrophilic nature are indicated (PolymerF reprint Japan 45 2922-2923 (1996)). However, the polymers of the above-mentioned statement have fluoride in structure, and usually (after desiccation) show water and oil repellency. Since it does not adapt itself to water immediately when these polymers are used for a coating agent for this reason, and oil contamination once adheres, in wiping by a wet rag etc., it is hard to remove dirt easily, and there is a problem. The invention which reforms surface character to hydrophilic oil repellency is indicated by JP,5-331455,A and JP,10-245419,A. However, the total monomers which each modifier given in these constitues do not have a vinyl group. The special polymerizing methods, such as making fluoride react to a silane compound (JP,5-331455,A), and dissolving a fluorene compound in a photopolymerization nature monomer (JP,10-245419,A), are needed. JP,5-331455,A has the statement of the thing which makes hydrophilic oil

repellency reveal by mixing an oil-repellent base and a hydrophilic group agent, and it is accompanied by the difficulty about pharmaceutical-preparationizing - the necessity of mixing uniformly two kinds of completely different bases of the compatibility over a solvent is in the top which needs the time and effort which manufactures two kinds of bases.

[0006]When JP,10-245419,A also polymerizes polymers, there is a manufacturing process of mixing the fluorene compound compounded beforehand. The part which processing beforehand at a place to use both gaseous (JP,5-331455,A, JP,10-245419,A) of both etc. operates has restriction. For this reason, it cannot be used easily but sufficient function can be revealed to no article surfaces at a place to use. The patent which gave

antifouling property using a water-and-oil-repellency base as a view of an easy cleaning system from the former is indicated by JP,5-414119,A and JP,6-279887,A. However, since these patents are water and oil repellency, once dirt adheres, the perviousness of water worsens and they cannot remove dirt easily by damping with a damp towel etc. Although the method of the conventional technology as an antifog processing agent processing the surface with a surface-active agent has been taken, it is temporary and neither of the methods reveals continuous fog resistance. For this reason, the invention which solicited durable fog resistance is indicated by JP,2000-192019,A and JP,9-59041,A. However, as these directions for using JP,2000-192019,A, heat-treat a coating surface at 140 °, and JP,9-59041,A cannot be easily used from the photocatalyst. The finishing agent using the polymers copolymer containing a sulfone group content hydrophilic nature vinyl monomer and a fluoro alkyl group content vinyl monomer is developed. For example, JP,63-106111,A other than above-mentioned JP,2-

147601,A and JP,7-34384,A is mentioned. However, inventions given in JP,63-106111,A are polymers which have

a graft chain (the daily doses of a side chain are 1000-100000) as an essential ingredient in polymers, and a use is also a dispersing agent for emulsion polymerizations.

[0007]

[Problem(s) to be Solved by the Invention]An object of this invention is to provide the fluoride content finishing

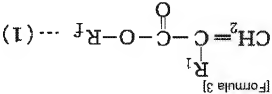
agent which can fully give antifouling property and fog resistance to a processed substrate. In spite of being able to process this invention, without receiving restriction of the kind of processed substrate, and the base material surface after coating treatment desiccation having the more outstanding antifouling property and fog resistance and being able to use it with a drainage system solvent moreover. Then, even if it contacts water, it is firmly fixed to the surface, and it aims at providing the fluoride content finishing agent which can prevent adhesion of dirt, dust, etc. and can remove the adhering thing easily. This invention only performs spreading etc. to further various processed substrate sides simply, and an object of this invention is to provide the antifouling property excellent in the substrate side, and fog resistance.

[0008]

[Means for Solving the Problem]This invention persons came to solve an aforementioned problem by using a polymers copolymer which consists of a specific vinyl monomer as a finishing agent, as a result of repeating research wholeheartedly that an aforementioned problem should be solved. That is, this invention attains the above-mentioned purpose by adopting composition of following the (1) - (5).

(1) A fluoride content finishing agent, wherein a fluoride system vinyl monomer (A) which has a fluoro alkyl group expressed with a following formula (1) contains a copolymer contained in the range of 1 - 70 mass % (finishing agent of the first this invention).

[0009]



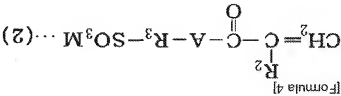
[0010]R₁ in a formula is hydrogen or an alkyl group of the carbon numbers 1-3, and R_f is an alkyl group which contains a fluorine atom in 2-31.

[0011](2) In the finishing agent of a statement, to the above (1) the above-mentioned copolymer, Besides the above-mentioned fluoride system vinyl monomer (A), tertiary amine or the 4th class ammonium content vinyl monomer (B), And a finishing agent, wherein it is a copolymer of both sexes amphiphilicity which contains an anionic vinyl monomer (C) as an essential ingredient and the ratios of ** (B) and (C) are 10 - 90-mol% in B/(B+C)

(finishing agent of the second this invention).

[0012](3) In the finishing agent of a statement, to the above (1) the above-mentioned copolymer, It is a copolymer of hydrophilic oil repellency which contains the sulfone group content hydrophilic nature vinyl monomer (D) expressed with a following formula (2) other than the above-mentioned fluoride system vinyl monomer (A) as an essential ingredient. The finishing agent containing ** (D) in this copolymer in the range of 20 - 95 mass %

[0013]



polymerization method. In this case, as a polymerization initiator, various kinds of publicly known things can be used conventionally. If it has the capability to start a radical polymerization, there will be no restriction in particular. For example, benzoyl peroxide, 2,2'-azobisisobutyronitrile, 2,2'-azobis (2-methylbutyronitrile), 2,2'-azobis (2,4-dibromoisobutyronitrile), 2,2'-azobis (2-amidinopropane) Two hydrochlorides, 2,2'-azobis (N,N'-dimethylmaleinylamide), potassium persulfate, ammonium persulfate, hydrogen peroxide, etc. are mentioned, and an azo compound is preferred. As a polymerization method, the publicly known polymerizing methods, such as solution polymerization, bulk polymerization, and a precipitation polymerization, are used. Although polymerization temperature changes with solvents to be used, generally it is 30 ° to 100 °, and polymerization time is 24 hours from 1 hour.

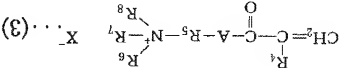
[0021] Thus, an average molecular weight of the above-mentioned polymers copolymer obtained has the preferred range of 1000 thru or 1 million, and this molecular weight is further limited by combination, the purpose, etc. of other monomers other than a fluorine system vinyl monomer (A). [0022] In the first this invention, although carrier fluid is made to distribute the above-mentioned fluoride content polymers copolymer and a finishing agent is provided, as for concentration of a fluoride content polymers copolymer in the finishing agent, it is preferred that it is 0.01 to 30 mass %, and it is 0.01 to 20 mass % more preferably. As for the above-mentioned finishing agent, it is preferred that it is a fluid, and, as for the above-mentioned fluoride content polymers copolymer, it is desirable to be able to make it distribute as an emulsion (granular, gel, and liquid in a fluid, and for it to be liquefied and to make it distribute stably especially. As carrier fluid, although water, an organic solvent, etc. can be mentioned, it is desirable that they are water, aqueous-phase solubility organic solvents, or these mixed solvents preferably. It shown in a finishing agent of the first this invention constituted in this way, antifouling property and fog resistance can fully be given to a processed substrate side.

[0023] In a finishing agent of the first this invention, one sort, such as anionic [of a detergent etc.], cationicity, nonionicity, and an ampholytic surface active agent, or two sorts or more may be used together. The above-mentioned finishing agent is independent, or it is used with a detergent and it can process a substrate side by spreading, immersion, or spraying. That is, in addition to antifouling property or fog resistance, detergency can be given by preparing a detergent for surface treatments containing the above-mentioned fluoride content polymers copolymer. In such a detergent for surface treatments, for example An anionic surface-active agent, Plasticizers (ethylene glycol etc.), chelating agents (EDTA etc.), solvents (ethanol etc.) and pH adjusters (citrate etc.), perfume besides surface-active agents, such as a cationic surface-active agent, a nonionic surface-active agent, and an ampholytic surface active agent, etc. can be used together. Under the present circumstances, it is good to make an anionic surface active agent and/or a nonionic surface active agent contain 0.01 to 10% in a detergent for hard surfaces.

[0024] Next, in a finishing agent concerning the second this invention the above-mentioned copolymer, Besides a fluorine system vinyl monomer (A), tertiary amine or the 4th class ammonium content vinyl monomer (B), And it is a copolymer of both sexes amphiphilicity which contains an anionic vinyl monomer (C) as an essential ingredient, and a ratio of (B) and (C) needs to 10 - 90-mol be % at B/(B+C), and can obtain a fluoride content polymers copolymer of both sexes amphiphilicity which was further excellent by this.

[0025] A vinyl monomer which has the at least one 4th class ammonium expressed with a following formula (3) or the 3rd class amino group as the above-mentioned tertiary amine or the 4th class ammonium content vinyl monomer (B) is preferred.

[0026]
[Formula 6]



However, the inside R₄ of the above-mentioned formula is shown, and the alkyl group of H or the carbon numbers

1-3, A, O or NH is shown, R₅ may show the straight chain shape or the branched state alkylene group of the

carbon numbers 1-8, and may also contain one or more hydroxyl groups, R₆ shows the alkyl group of H or the

carbon numbers 1-12, and R₇ and R₈ show the alkyl group of the carbon numbers 1-12, X⁻ shows counteranion,

in particular, although application of a chloride and a bromide is preferred, it is not necessary to need

counteranion depending on the case. As this example, chloridation dimethylamino ethyl acrylate, chloridation

dimethylaminoethyl methacrylate, Dimethylaminoethyl acrylamide chloride, chloridation diethylamino ethyl

acrylate, Chloridation diethylaminoethyl methacrylate and diethylaminoethyl acrylamide chloride, Chloridation dimethylamino pro

pyl methacrylate, dimethylaminoethyl chloridation methacrylate, Chloridation dimethylamino pro

pyl methacrylate, Chloridation dimethylaminoethyl acrylate, Chloridation dimethylaminoethyl methacrylate,

Chloridation trimethylaminoethyl acrylate, Chloridation trimethylaminoethyl methacrylate, Chloridation trimethyl

aminoethyl acrylate, chloridation 1-trimethyl amino-2-hydroxypropyl methacrylate, [3-(meta-acrylic amino) propyl

aminoethyl acrylate, chloridation 1-trimethyl amino-2-hydroxypropyl methacrylate, [3-(meta-acrylic amino) propyl

aminoethyl acrylate, chloridation 1-trimethyl amino-2-hydroxypropyl methacrylate, [3-(meta-acrylic amino) propyl

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aminoethyl acrylate, chloridation 1-trimethyl amino-2-hydroxypropyl methacrylate, [3-(meta-acrylic amino) propyl

aminoethyl acrylate, chloridation 1-trimethyl amino-2-hydroxypropyl methacrylate, [3-(meta-acrylic amino) propyl

content vinyl monomer (B), and an anionic vinyl monomer (C) — B/(B+C) — 10 - 90-mol% — preferably, 20-85-mol%, is 30-75-mol% more preferably, and cannot fully perform revealing performance made into the purposes, such as antifouling property and fog resistance, out of 10-90-mol% of the range of the above-mentioned setting-out ratio.

[0030] In the second this invention, since copolymers of above-mentioned vinyl monomer (A) - (C) are both sexes amphiphilic polymers, the above-mentioned finishing agent can be provided with a drainage system solvent. Concentration of the above-mentioned copolymer in the above-mentioned finishing agent is 0.1 to 15 mass % preferably [that is 0.1 to 20 mass %], and more preferably, if the above-mentioned copolymer contains in a finishing agent within the limits of 0.01 - 20 mass %, sufficient antifouling effect and the antifog effect can be demonstrated. Although it is preferred that it is a drainage system solvent gestalt as for the above-mentioned finishing agent, a drainage system solvent in water itself ***** , it may be drainage system solvent, such as lower alcohol, oxide, and ketone (aqueous-phase solubility organic solvent), a mixed solvent of those, etc., and each solvent can be added in the range which does not have an adverse effect on the solubility of the above-mentioned copolymer, and stability, or it can be used. The finishing agent of the second this invention can use together one sort, such as anionic [or a detergent etc.], cationicity, nonionicity, and an amphoteric surface active agent, or two sorts or more like the first this invention. The above-mentioned finishing agent is independent, or it is used with a detergent and it can process a substrate side by spreading, immersion, or spraying.

[0031] When a fluorine content finishing agent concerning the second above this invention is used for the surface treatments of a variety and various processed substrates, a further outstanding treatment effect is demonstrated. Especially the above-mentioned copolymer is contained as a constituent of a drainage system solvent, and can be easily coated on the surface of a substrate. This does not receive restriction of a kind of processed substrate, but has the outstanding antifouling property, moreover, in spite of use of a drainage system solvent, even if it contact water after that, it is firmly fixed to the surface and prevents adhesion of dirt and dust. It is easily removable even if it adheres.

[0032] That is, use of a drainage system solvent is possible for the above-mentioned fluoride content polymers copolymer used for the second this invention as carrier fluid, and a drainage system solvent functions as stable carrier fluid or a fluoride content polymers copolymer. Therefore, a finishing agent concerning the second this invention can be used by drainage system solution states, and soft surfaces, such as hard surfaces, such as stainless steel, glass, and various plastics, and hair, and textiles, are mentioned as the processing-object surface. The above-mentioned finishing agent prevents adhesion of dirt of these surfaces and dust, or removes an adhering thing simply. From this the above-mentioned fluoride content polymers copolymer, it has a function also as a surface treatment ingredient in liquid detergents for dwellings, such as detergents for textiles, such as hair and detergents for the bodies, such as a shampoo, rinse, and soap, and cosmetics, a curtain, and furniture made of cloth, a kitchen, a range, a tile, a bus, glass, a mirror, a wooden furniture, a floor, and a household appliance, and a home detergent.

[0033] In a finishing agent which furthermore starts the third this invention, the above-mentioned copolymer, it is a monomer (D) other than the above-mentioned fluorine system vinyl monomer (A) as an essential ingredient. The film characteristic of this copolymer is a copolymer which are 45 degrees or less of angles of contact with water, and not less than 65 degrees of angles of contact with vegetable oil (surface tension about 30 mN/m), and it is a copolymer of hydrophobic oil repellency which the above (D) contains in this copolymer in the range of 20 - 95 mass %. In the above-mentioned copolymer, if an angle of contact with water exceeds 45 degrees, a wet dustcloth etc. cannot wash easily. Oil contamination reaches powerfully that an angle of contact with vegetable oil is less than 65 degrees, and it cannot wash easily. As the above-mentioned sulfone group content hydrophobic nature vinyl monomer (D), at least one or more sorts of vinyl monomers expressed with a following formula (2) are

mentioned.

[0034]

[Formula 7]

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[0035] In the above-mentioned formula is hydrogen or an alkyl group of the carbon numbers 1-3, and here A, is O or NH, R³ is the carbon numbers 1-15 especially the straight chain shape of 1-10, a branched state alkylene group, or an alkenylene group, and M is hydrogen, alkali metal salt, or an ammonium derivative.

[0036] As the above-mentioned sulfone group content hydrophilic nature vinyl monomer (D), For example, acrylamide methanesulfonic acid, acrylamide ethane sulfonic acid, Methanesulfonic acid acrylate, ethane-sulfonic-acid acrylate, acrylamido propanesulfonic acid, 2-acrylamido-2-methyl propane sulfonic acid, 2-methacrylamide 2-methylpropanesulfonic acid, 2-acrylamide n-butanedisulfonic acid, etc. are mentioned. 2-acrylamido-2-methyl propane sulfonic acid etc. are preferred especially among these sulfone group content hydrophilic nature vinyl monomers (D).

[0037] As these sulfone groups, not only an acid type but its salt is contained. The salt may be used together with independent or an acid type, and copolymerization may be carried out. As a salt of a sulfone group content monomer, organic amine salt, such as each alkali metal salt, ammonia, triethylamine, triethanolamine, and monethanolamine, etc. are mentioned. It is good also as the above-mentioned fluoride content polymers copolymer for alkali chemicals to neutralize a sulfone group content monomeric unit of a copolymer obtained.

[0038] The above-mentioned fluoride content polymers copolymer in the third this invention may carry out copolymerization of other monomers other than a fluorine system vinyl monomer (A) and a sulfone group content vinyl monomer (D). As a kind of monomer, the two above-mentioned sorts of monomers and copolymerization are possible, and it will not be limited especially if it is a monomer which does not affect hydrophilic oil repellency. As a kind of such a monomer, a hydrophobic vinyl monomer (E), a nonionic hydrophilic monomer (F), and an ionicity vinyl monomer (G) are mentioned. Tertiary amine mentioned above or a quaternary-ammonium-salt content vinyl monomer (B), and an anionic vinyl monomer (C) can be mentioned to an ionicity monomer (G), and the detailed explanation is omitted.

[0039] As the above-mentioned hydrophobic vinyl monomer (E), methyl acrylate, methyl methacrylate, Ethyl acrylate, ethyl methacrylate, butyl acrylate, butyl methacrylate, 2-ethylhexyl methacrylate, 2-cyclohexyl methacrylate, decyl acrylate, decyl methacrylate, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl acrylate, 2-hydroxypropyl methacrylate, 3-hydroxypropyl acrylate, 3-hydroxypropyl methacrylate, 2-hydroxy-3-phenoxypropyl acrylate, 2-hydroxy-3-phenoxypropyl methacrylate, etc. are mentioned.

[0040] As a nonionic hydrophilic monomer (F), Acrylamide, methacrylamide, polyethylene-glycol acrylate (degrees of polymerization 1-30 of ethylene oxide), Polyethylene-glycol methacrylate (degrees of polymerization 1-30 of ethylene oxide), Methoxy polyethylene-glycol acrylate (degrees of polymerization 2-30 of ethylene oxide), methoxy polyethylene-glycol methacrylate (degrees of polymerization 2-30 of ethylene oxide), etc. are mentioned.

[0041] Also in the above-mentioned fluoride content polymers copolymer in the third this invention, the above-mentioned fluoro alkyl group content vinyl monomer unit (A) needs to be 1-70 mass % included, and is 2-60 mass % preferably. In the above-mentioned fluoride content polymers copolymer, a sulfone group content hydrophilic nature vinyl monomer unit (D) needs to be 25-95 mass % included, and is 30-95 mass % preferably.

in the above-mentioned fluoride content polymers copolymer, as for quantity of the above-mentioned hydrophobic monomer (E), a nonionic hydrophobic monomer (F), and an ionic monomer (G), 0-30 mass % being contained is preferred as the whole quantity, and it is 0 - 25 mass % more preferably. The above-mentioned fluoride content polymers copolymer may be a random copolymer or block copolymer for above-mentioned (A) - (G) ingredient.

[0042]As the above-mentioned fluoride content polymers copolymer, what shows at least 1000 or more average molecular weight from a point of film nature is preferred, and a thing of 1 million or less molecular weight is preferred from solubility over a solvent. It is 2000-800,000 more preferably.

[0043]Like the first this invention, the third this invention makes carrier fluid distribute the above-mentioned fluoride content polymers copolymer, and provides a finishing agent. As for concentration of a fluoride content polymers copolymer in the finishing agent, it is preferred that it is 0.01 to 30 mass %, and it is 0.01 to 20 mass % more preferably. As for the above-mentioned finishing agent, it is preferred that it is a fluid, and, as for the above-mentioned fluoride content polymers copolymer, it is desirable to be able to make it distribute as an emulsion (granular), gel, and liquid in a fluid, and for it to be liquefied and to make it distribute stably especially. As carrier fluid, although water, an above-mentioned organic solvent, etc. can be mentioned, they are water, aqueous-phase solubility organic solvents, or these mixed solvents preferably. If shown in a finishing agent constituted in this way, antifouling property and fog resistance can fully be given to a processed substrate side. The finishing agent of hydrophobic oil repellency of the third this invention can use together one sort, such as anionic [of a detergent etc.], cationicity, nonionicity, and an amphoteric surface active agent, or two sorts or more like the first this invention. The above-mentioned finishing agent is used with an independent or above-mentioned detergent, and can process a substrate side by spreading, immersion, or spraying.

[0044]Outstanding dirt removal nature (antifouling property) and fog resistance can be given by making the object surface process the above-mentioned hydrophobic oil repellency finishing agent. Under the present circumstances, as the object surface, glass, earthenware, a plastic, a floor, textiles, polyester, acrylic products, the skin, hair, paper, ABS plastics, etc. are mentioned. Therefore, when the above-mentioned fluoride content polymers copolymer reforms the processed substrate side to hydrophobic oil repellency, it is possible to make further outstanding dirt removal nature (antifouling property) and fog resistance reveal.

[0045]

[Example]Next, this invention is further explained in full detail according to an example and a comparative example. This invention is not restricted to these examples at all. First, a fluorine system vinyl monomer (A), tertiary amine or the 4th class ammonium content vinyl monomer (B), and an anionic vinyl monomer are used for

Example 1 thru/for Example 10.

[0046]To separable FURAKO which attached <Example 1> cooling refluxing pipe, a thermometer, a nitrogen introducing pipe, and agitating equipment, 2-acrylamido-2-methyl propane sulfonic acid (AMPS) : 36 g,

Methacrylic acid dimethylamino ECHIRUMÉ chll chloride salt (DMC) : 9 g, 1 H, 1 H, 2 H, 2 H-heptadecafluoro decyl acrylate (17F) : 5 g, 10.8 g of monoethanamine, the 2,2-azobis (2-amidinopropane) hydrochloride 0.59g, and 200 g of ethanol/exchange water (= 70/30wt%) were prepared, and it stirred for 30 minutes at the room

temperature, blowing nitrogen. Temperature up of the system of reaction was carried out to 85 °, and the reaction was performed for 6 hours. Output was picked out from the reactor and 45g of solids of polymers was obtained by making it reprecipitate by hexane. The average molecular weight of the obtained polymers was 150,000. Other polymers other than Examples 9 and 10 and comparative example 3 were manufactured by the

same polymerizing method as the above.

[0047]<Example 2> monomer - 2-acrylamido-2-methyl-p-propane-sulfonic-acid (AMPS) : - 20 g, Methacrylic-acid dimethylamino ECHIRUMÉ chll chloride salt (DMC): It was referred to as 10 g and 1 H, 1 H, 4 H, 4 H-octadecylpropanoic methacrylate (8FM):20g, and polymerized on the same conditions as Example 1 except having put in

monoethanamine:6g.

<Example 3> monomer - 2-acrylamido-2-methyl-propane-sulfonic-acid (AMPS): - 30.5 g. Methacrylic-acid dimethylamino ECHIRUMÉ chll chloride salt (DMC): It was referred to as 14.5 g and 1 H,1 H,2H-octylfluoropentyl acrylate (6F):5g, and polymerized on the same conditions as Example 1 except having put in monothalamine:9.2g.

[0048]<Example 4> monomer - methacrylic acid (MAA): - It polymerized on the same conditions as Example 1 except having been referred to as 3 g, dimethylaminoethyl methacrylate (DM):22g, and 1 H,1 H,2 H,2H-heptadecafluorodecyl methacrylate (17FM):25g.

<Example 5> monomer - methacrylic acid (MAA): - It polymerized on the same conditions as Example 1 except having been referred to as 5.5 g, dimethylaminoethyl methacrylate (DM):29.5g, 2, 2 and 3, and 3-

tetrafluoropropylacrylate (6MF):15g.

<Example 6> monomer - 2-acrylamido-2-methyl-propane-sulfonic-acid (AMPS): - 6.75 g. Methacrylic amnopoly trimethylammonium chloride (MAPTA): It was referred to as 16.75 g and 2,2,2-trifluorethyl acrylate (6F):1.25g, heptadecafluorodecyl methacrylate (17FM):2g.

<Example 8> monomer - 2-acrylamido-2-methyl-propane-sulfonic-acid (AMPS): - 36 g. Methacrylic amnopoly trimethylammonium chloride (MAPTA): It was referred to as 12.75 g and 2,2,2-trifluorethyl acrylate (6F):1.25g, [0050]To separable FURAKO which attached <Example 9> cooling refluxing pipe, a thermometer, a nitrogen introducing pipe, and agitating equipment, 2-acrylamido-2-methyl propane sulfonic acid (AMPS): 41.5 g, methacrylic amnopoly trimethylammonium chloride (MAPTA): 7.75 g, 1H, 1H, 5H-octylfluoropentyl

methacrylate (6FM): 0.75 g, It stirred for 30 minutes at the room temperature, having prepared 12.5 g of monoethanolamine, the 2,2-azobis (2-amidinopropane) hydrochloride 0.45g, and 90 g of ethanol exchange

water (= 70/30wt%), and blowing nitrogen. Temperature up of the system of reaction was carried out to 55 °, and the reaction was performed for 14 hours. Output was picked out from the reactor and 47g of solids of polymers were obtained by making it reprecipitate by hexane. The average molecular weight of the obtained polymers was 1,400,000.

[0051]To separable FURAKO which attached <Example 10> cooling refluxing pipe, a thermometer, a nitrogen introducing pipe, and agitating equipment, 2-acrylamido-2-methyl propane sulfonic acid (AMPS): 3 g, Methacrylic acid dimethylamino ECHIRUMÉ chll chloride salt (DMC): 18 g, 1 H,1 H,2 H,2H-heptadecafluorodecyl methacrylate (17FM): 29 g, It stirred for 30 minutes at the room temperature, having prepared 0.9 g of monoethanolamine, the 2,2-azobis (2-amidinopropane) hydrochloride 2.12g, and 450 g of ethanol exchange

water (= 70/30wt%), and blowing nitrogen. Temperature up of the system of reaction was carried out to 85 °, and the reaction was performed for 4 hours. Output was picked out from the reactor and 41g of solids of polymers were obtained by making it reprecipitate by hexane. The average molecular weight of the obtained polymers was 8000.

[0052]the <comparative example 1> monomer - methacrylic acid (MAA): - It polymerized on the same conditions as Example 1 except having been referred to as 0.5 g and methacrylic acid dimethylamino ECHIRUMÉ chll chloride salt (DMC):49.5g.

the <comparative example 2> monomer - 2-acrylamido-2-methyl-propane-sulfonic-acid (AMPS): - It polymerized on the same conditions as Example 1 except having been referred to as 0.5 g and methacrylic acid

dimethylamino ECHIRUMÉ chll chloride salt (DMC):49.5g.

the <comparative example 3> monomer - 2-acrylamide isobutane sulfone (AMPS) acid: - 48 g,

Dimethylaminoethyl-methacrylate (DM): 1.75g, 1 H,1 H,2 H,2H-heptadecafluorodecyl acrylate (3FM): 11

polymerized on the same conditions as Example 10 except having been referred to as 0.25 g. The presentation and physical properties of a constituent in the above example and comparative example are shown in the following table 1.

[Table 1]

分子種	分子種	7素E7-最	(%対%)	(%)	カチオン
実施例 1	AMP5/DHC/17	F	10	80/20	
実施例 2	AMP5/DHC/8P	M	40	67/33	
実施例 3	AMP5/DHC/8P	M	10	68/32	
実施例 4	MAA/DH/17FM		15	20/80	
実施例 5	MAA/DH/6FM		15	26/74	
実施例 6	AMP5/MAPTAC		15	30/70	
実施例 7	MAA/DH/17FM		15	40/60	
実施例 8	AMP5/MAPTAC		15	75/25	
実施例 9	AMP5/MAPTAC		140	85/15	
実施例 10	AMP5/DHC/17	FM	8	14/86	
比較例 1	MAA/DHC		15	2/98	
比較例 2	AMP5/DHC		15	1/99	
比較例 3	AMP5/DH/3FM		140	0.5	97/3

[0054]Next, in accordance with the following valuation methods, the evaluation test was done for the constituent obtained by the above-mentioned example and the comparative method is as follows and shows the result in Table 2 and 3.

[0055]Using the polymers copolymer obtained by the <antifouling property evaluation 1> example and the comparative example, it blended so that macromolecule concentration might become 5 mass %, and after spreading and desiccation and vegetable oil were used for 2.5x7.5-cm slide glass for this constituent, and that antifouling property was judged visually. The standard is as follows.
O : - completely - oil-contamination-less O : - almost - oil-contamination-less *: - using the polymers copolymer and active agent solution which were obtained for a white by the example with [with oil contamination / x] oil contamination <the antifouling property evaluation 2>, and the comparative example, Lauryldimethyl betaine aminoacetate : 0.07 mass %, lauryl ethoxy sulfate: 0.17 mass %, Ethanol: It blended so that macromolecule concentration might become 5 mass %, and after spreading and desiccation and vegetable oil were used for 2.5x7.5-cm slide glass for this constituent, and that antifouling property was judged visually. The

standard is as follows.

O : — completely — oil-contamination-less O : — almost — oil-contamination-less ** : — a few — those with x:oil contamination with oil contamination [0056] in order to evaluate the antioffing property of the <adhesion [of carbon black] remaining evaluation 1> solid pollutant, apply each sample whose macromolecule concentration is 5% and are water and it rinses. After performing distance discarded once it sprinkles carbon black, the visual judgment of the adhesion condition of carbon black after washing in cold water again was carried out on the following standards.

O : — O : which carbon black does not attach at all — ** : which carbon black hardly attaches — x : which remains slightly, in order to evaluate the antioffing property of the <adhesion [of carbon black] remaining evaluation 2> solid pollutant currently attached considerably. Lauryldimethyl betaine aminoacetate : 0.07 mass % lauryl ethoxy sulfate:0.17 mass %, Ethanol: After performing distance discarded once it applies to 5 mass % the sample whose macromolecule concentration is 5%, and is water, it rinses and it sprinkles carbon black, the visual judgment of the adhesion condition of carbon black after washing in cold water again was carried out on the following standards.

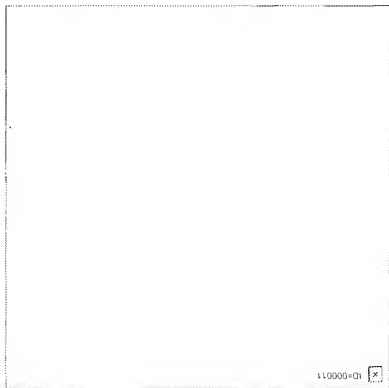
O : — O : which carbon black does not attach at all — ** : which carbon black hardly attaches — x : which remains slightly — attach considerably[0057] in order to evaluate the antioffing property of the <antioffing evaluation 1 of textiles> thing, after infiltrating into a towel each sample whose macromolecule concentration is 5% and drying, 2 g of red chili pepper oil was infiltrated. Then, the washing machine washed and the visual judgment of red chili pepper oil was carried out on the following standards.

O : — O : which red chili pepper oil does not attach at all — ** : which red chili pepper oil hardly attaches — x : which remains slightly — attach considerably [0058] it blended so that the macromolecule concentration obtained by the visual judgment of the adhesion condition of red chili pepper oil was carried out on the following standards. mass % is 5% and drying, 2 g of red chili pepper oil was infiltrated. Then, the washing machine washed and the sample whose macromolecule concentration of 0.07 mass %, lauryl ethoxy sulfate:0.17 mass %, and ethanol:5 thing currently attached considerably, Lauryldimethyl betaine aminoacetate: After infiltrating into a towel the remains slightly, in order to evaluate the antioffing property of the <antioffing evaluation 2 of textiles> textiles

O : — O : which red chili pepper oil does not attach at all — ** : which red chili pepper oil hardly attaches — x : which remains slightly — attach considerably [0059] it blended so that the macromolecule concentration obtained by the visual judgment of the adhesion condition of red chili pepper oil was carried out on the following standards. mass % is 5% and drying, 2 g of red chili pepper oil was infiltrated. Then, the washing machine washed and the sample whose macromolecule concentration of 0.07 mass %, lauryl ethoxy sulfate:0.17 mass %, and ethanol:5 thing currently attached considerably, Lauryldimethyl betaine aminoacetate: After infiltrating into a towel the remains slightly, in order to evaluate the antioffing property of the <antioffing evaluation 2 of textiles> textiles

standards.

ID=000011



[0060]

[Table 3]

サンプル	防汚性 2	付着残りの 繊維の防汚 性 2	防汚評価 2
実施例 1	◎	◎	○
実施例 2	◎	◎	◎
実施例 3	◎	◎	◎
実施例 4	○	○	○
実施例 5	◎	◎	◎
実施例 6	◎	○	○
実施例 7	◎	◎	◎
実施例 8	○	◎	○
実施例 9	○	○	○
実施例 10	○	○	○
比較例 1	×	×	×
比較例 2	×	×	×
比較例 3	×	×	×

[0061] As mentioned above, it turns out that the finishing agent by Examples 1-10 is excellent in antifouling

property and fog resistance from the result. On the other hand, it is in a comparative example, antifouling

property and fog resistance are hardly seen, and even if it uses a fluorine system monomer like the comparative

example 3, sufficient effect will not be acquired if there are few the additions. Since it turns out that especially the finishing agent by Examples 1-8 is excellent, a fluoride monomer amount is understood that 2.0 to 55% of within the limits is still more preferred. The molecular weight of a polymers copolymer is understood that the thing of hundreds of thousands orders is desirable.

[0062] Next, a fluorine system vinyl monomer (A) and a sulfone group content vinyl monomer (D) are used for Example 11 thru/ or Example 20.

(Presentation of a fluoride content polymers copolymer) That mass % shows the composition ratio of a fluoride type polymers copolymer, an anionic monomer shows an acid type and a basic monomer indicates the H-ion ratio to be was calculated as an N-ion type, and the 4th class salt type monomer was calculated as composition ratio when a chloride is used for a counter ion.

[0063] The fluoride content polymers copolymer of the following (1) - (10) was used for Examples 11 thru/ or 20. (11) and (12) were used for the comparative examples 4 and 5.

(1) Fluoride content polymers copolymer 1: 2-methyl-2-acrylamide propanesulfonic acid. (AMP/S) 1/1 H, 1, 2 H, 2, 4-heptadecafluorodecylmethacrylic acid (17FMA) = 90/10(2) fluoride content polymers copolymer 2: AMP/S/17FMA = 60/40(3) fluoride content polymers copolymer 3: AMP/S/14, 14, 5H-octylfluoropentyl acrylate. (8FAA) = 70/30. Fluoride content polymers copolymer 4: AMP/S/17FMA / methyl methacrylate (MMA) = 35/40/25(5) fluoride content polymers copolymer 5: AMP/S/17FMA / butyl methacrylate (BMA) = (4) 40/55/5. (6) Fluoride content polymers copolymer 6: AMP/S/2,2,2-trifluoroethylmethacrylate (3FMA) / MMA = 35/55/10(7) fluoride content polymers copolymer 7: AMP/S/17FMA / methacrylic acid (MAA) = 40/40/20 [0064] (8) fluoride content polymers copolymer 8: AMP/S/8FAA / dimethylaminoethyl methacrylate (DMA) = 50 / 30 / 20(9) fluoride content polymers copolymer 9: AMP/S/8FAA / acrylic acid (AA) = 35/45/20. (10) fluoride content polymers copolymer 10: AMP/S-KURIRITO = 40/35/10/10/10/methylaminoethyl methacrylate chloride / methoxy polyether (p = 23) meta-5 (11) styrene/MMA/BMA/MAA = 25/40/27/8 [0065] To separable FURAKO which attached a example of the polymerization of fluoride content polymers copolymer 4< cooling refluxing pipe, a thermometer, a nitrogen introducing pipe, and agitating equipment. AMP/S 17.5g, MMA 12.5g, 17FMA 20g, 5.1 g of monoethanolamine, it started at the room temperature for 30 minutes, having prepared the 2,2-azobis (2-amidinopropane) hydrochloride 0.69g, and 200 g of ethanol/ ion exchange water (= 80/20wt%), and blowing nitrogen. Temperature up of the system of reaction was carried out to 55 **, and the reaction was performed for 6 hours. Output was picked out from the reactor and 45g of solids of polymers were obtained by making it reprecipitate by hexane. The average molecular weight of the obtained polymers was 40,000. They were 20 angles of contact of water, and 85 angles of contact of vegetable oil. Other polymers other than polymers 12 were manufactured by the same polymerizing method as the above.

[0066] It carried out like the time of the polymers 4 except having used acetone for the <example of the polymerization initiator>. The average molecular weight of the obtained polymers was 30,000. They were 74 angles of contact of water, and 28 angles of contact of vegetable oil.

[0067] Hereafter, the solvent used for evaluation prepared the sample for evaluation using ethanol/ ion-exchange water = 80 / 20 (wt%). Although the stainless plate was used for the example of the hard surface substrate, glass, earthenware, a plastic, a tile, a floor, etc. are the same, and it does not limit in particular. Although the cotton of clothing was used for the example of soft surface materials, polyester, acrylic products, vinyl products, the skin, hair, etc. are the same, and it does not limit in particular.

[0068] It prepares so that < dirt removal nature (antifouling property) evaluation of hard surface substrate (stainless steel) > copolymer concentration may be 5%, and 0.3mL spreading was carried out and the stainless plate (2 cm x 6 cm) was dried. Vegetable oil was hung down to this board at 4 or 5 places, the board was put, and water was

poured. The three-stage estimated omission of the oil at that time by viewing.
 3. it falls well. it falls by 2; half. 1; it does not fall.

[0069] it prepares so that < dirt removal nature (antifouling property) evaluation of soft surface (clothing) >

macroscopic concentration may be 5%, and 0.5mL spreading was carried out and the cotton of 5 cm around was dried. Dirt was 0.1 mL-hung down to this cotton, and it was made to dry it. Water was prepared so that a bath ratio might be set to 50, using the commercial detergent (made by Lion company), it added so that detergent concentration might be set to 2000 ppm, it washed for 10 minutes, and it dried, after rinsing. The three-stage estimated omission of the dirt at that time by viewing.
 3. it falls well. it falls by 2; half. 1; it does not fall.

[0070] 1mL spreading of the polymer solution of concentration 1 mass % or the dispersion liquid was carried out at the <log resistance evaluation > sample preparation glass plates (10 cm x 10 cm), and it was made to wipe and dry using KIMUWAIPIU. On the water which has boiled this glass plate, to the field of water, the processed field was turned to the water side and settled on the place 10 cm high, at the angle of 60 degrees. Viewing estimated surface appearance by the three-stage.

more than which blooms cloudy is shown in Table 4, 5, and 6.

[0071]

[table 4]

実施例 11	実施例 12	実施例 13	実施例 14	実施例 15
フッ素含有分子 (1)	(2)	(3)	(4)	(5)
水の接触角 20°	20°	16°	14°	19°
セラミズの接触角 83°	85°	80°	85°	82°
硬表面の防汚性	3	3	3	3
軟表面の防汚性	3	3	3	3
軟表面の防汚性	3	3	3	3
防曇性	3	3	3	3

[0072]

[table 5]



[0073]

[table 6]

比較例 5	比較例 4	
フッ素含有成分率	(1 1)	(1 2)
共重合体		
水の接触角	25°	74°
セラグ油の接触角	25°	28°
離表面の防汚性	1	1
軟表面の防汚性	1	1
防曇性	2	1

[0074]As mentioned above, it turns out that a result and Examples 11 thru/ or 20 give antifoiling property and fog resistance excellent in the substrate side. And it turns out that this substrate side fully holds hydrophilic oil repellency. Therefore, by making the object surface process the above-mentioned fluoride content polymers copolymer, the outstanding dirt removal nature (antifoiling property) and fog resistance can be given, and grant of hydrophilic oil repellency can fully be performed.

[0075]

[Effect of the invention]As explained above, since the fluorine system vinyl monomer (A) which has a fluoro alkyl group expressed with the above-mentioned formula (1) contains the copolymer contained in the range of 1 - 70 mass %, the fluoride content finishing agent concerning this invention can fully give antifoiling property and fog resistance to a processed substrate.

[Translation done.]

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(54) 発明の名称 ツッ素含有表面処理剤

(57) 【要約】
【課題】 被処理基材に防汚性及び防曇性を十分に付与することのできるツッ素含有表面処理剤及びその表面処理剤を提供すること。
【解決手段】 本発明のツッ素含有表面処理剤は、下記式(1)で表されるツッ素含有表面処理剤を有するツッ素系ニルモノマー(A)が1〜70質量%の範囲で含まれる共重合体を含有する。
【化1】
$$\text{CH}_2=\text{C}(\text{R}_1)-\text{C}(=\text{O})-\text{O}-\text{R}_f \cdots (1)$$

(式中のR1は、水素、或いは炭素数1〜3のアルキル基であり、Rfは、ツッ素原子を2〜31の範囲で含むアルキル基である。)

種以上を組み合わせ、1種用いても良いし、2
 ユクロロ4ノ下等が挙げられ、1種用いても良いし、2
 ー(A)～(C)の共重合体は両性両親媒性高分子であ
 るため、上記表面処理剤は水系塗料で提供することがで

【0028】第二の実例に用いられる共重合体における、 α -アノニオン性モノマー(C)としては、例えば、0.1～20重量%であるのが好ましく、より好ましくは、さる、上記表面処理剤中の上記共重合体の濃度は、0.

後述するニルアルボン酸、7リルアルボン酸、 α -ナ
ニルアルボン酸、 α -ニルアルボン酸、 α -7リルアル
0.1~1.5質量%である。0.01~20質量%の範囲
図6で下記重合物体が平面状複層に含有されてい

ミフ-2-メチルプロピルノ酸等のアルホノ酸類
 十分な防汚効果及び防食効果を発揮することができ、
 また、上記表面処理剤は、水溶液状態であることが好ま

3カ月を(×8)7カ月と表記する。7カ月

ピニルホス、等々のカルボキシル基類、
ピニルホスアノエー、アジツクホス
の水系溶媒及びその混合溶液などであっても良く、上記

[illegible]

酸類又はアルキルホリン酸その塩が好ましく、更に好ましくは (X9) 下リル酸、2-下リル下ミド-2-メチルアミノエチル、カチオン性、ノニオン性、両性界面活性剤

フタバスルホネ酸である。チオソジ性でニルモノラ
一、は、単独で用いても良いし、２種以上を組み合わせ
面処理剤は単独又は洗浄剤と共に用いられ、塗布、浸

て用いても良い。また、本発明で用いられているアノソ性⁽²⁾ニルモノ⁽¹⁾は、その塩または酸との混合物の形で用いても良い。

濃、或いは噴霧などによって基材面の処理をすることが出来る。

で用いることもできる。これらの塩には、アルカリ金属塩、アゼモニウムやトリエチルアミン、トリエノール塩の他、アゼモニウム塩や、多量、少量の有機溶媒を含む有表面処理液、多量、少量の有機溶媒を含む表面処理液

ルアリソ等の塩基性化合物との酸を発生することができ
に用いたとき、更に優れた処理効果を発揮する。特に、
上野共済會社は水系腐蝕の阻成剤として含有され、薬材

[illegible]

分子共融割合は、(A)、(B)、(C)とラジカル重合
ち、しかも水系溶液の使用にもかわらず、その後、水

い。上記ア、薬時効減少分/生体液体の平均分子量は、1

～100万が好ましく、更には5000～80万とする
【0032】即ち、第二の本発明に用いる上記7つの割合

のふよい、分子量が150万を超えらるものでは粘度が非常に高くなり、分子量が1万以下になると流動性が高くなり、分子量が1万と150万の間で重合したものは、分子量が増えるにつれて粘度も増える。このように、分子量の異なる重合体を混合して用いることが可能であり、水素飽和は7つの場合があり、重合時分割水素命令の決定な

0.00未満のものは目的とする性能を発現することが分岐線として機能する。従って、第二の本発明に係る表面処理剤は水系溶液状態で使用することができ、その処

【0029】第二の本発明においては、第一の本発明と同様に、上記共重合体中のフルオロアルキル基を有するナフなどの環表面、及び毛髪や繊維などの数表面が塗

上記7ヶ国系ビルモ/ゾー(A)は、その7-100割
量当たり、1-70割量%、特に1-60割量%、好
みの付着を防止したり、付着したものを簡単に除去す
けられる。上記表面処理剤は、これら表面の汚れやコ

ましくは2～5%減量%、より好ましくは3～5%減量%であり、70%減量%を超える場合は水系溶液に対するヤブブー、リッス、石鹸などの手洗・身体用洗剤及びる、このことから上記7%含有高分子共重合体は、シ

溶媒性を低くし、また1質量%未満では防汚性、防曇性を確保する。また、性質を制御するポイントがいくつかあり、台所、リビング、トイレ、バス、玄関、本棚など、化粧品、衣料、カーテン、市販家具などの繊維用洗浄

る。上記3款^①のミ、または4款^②のミにのみ適合して、
ニルホ^③（ゾー）^④、アノニホ^⑤（ゾー）^⑥、
ル、ア、刺鶴銀に使用致す等理、及び刺鶴用等事に
於ける製造管理に於ては、適合する。

【0033】更に第三の本発明に係る表面処理剤におい

上記設定比率の10～90mol%の範囲外では、防汚

分には出来ない。

【0030】第一の本発明において、上記エニル基の平均分子量は、45以下、499未満（表面張力約30mN/m以下）である。

メチルアミンニ酸化クロライド (MAPTA) : 1.75
 g, H₂1H, 5H-オキソノ交水 (=70/30mL%) 90gを仕込
 び、エタノール/(2-アミジプロピル)ノイソクロライド
 (FPM) : 0.75g, モノエノールアミン/2.5g, 2.2-
 アセトニルアミン/2.5g, 2.2-アセトニルアミン/2.5g
 を55℃に昇温して14時間反応を行った。生成物を反応
 素を吹き込みながら室温で30分間攪拌した。反応
 素を吹き込みながら室温で30分間攪拌した。反応素を85
 ℃に昇温して4時間反応を行った。生成物を反応器から
 取り出し、ヘキサンで再沈澱させることにより高分子の
 固体を41g得た。得られた高分子の質量平均分子量は800
 0であった。
 【0052】 <比較例1> モノアミンをメチルアミン
 (MA) : 0.5g, メチルアミン酸シメチルアミン/エチル
 メチルクロライド (DMC) : 49.5gとした以外は実
 施例1と同じ条件で重合を行った。
 <比較例2> モノアミンを2-アミジプロピルアミン/2-メ
 チルアミン/2-メチルアミン/エチルアミン/クロライド (DM
 C) : 49.5gとした以外は実施例1と同じ条件で重合を
 行った。
 <比較例3> モノアミンを2-アミジプロピルアミン/2-メ
 チルアミン/2-メチルアミン/エチルアミン/クロライド (DM
 C) : 49.5gとした以外は実施例1と同じ条件で重合を行
 った。
 <比較例4> モノアミンを2-アミジプロピルアミン/2-メ
 チルアミン/2-メチルアミン/エチルアミン/クロライド (DM
 C) : 49.5gとした以外は実施例1と同じ条件で重合を行
 った。
 【0053】
 物性を以下の表1に示す。

サンプリ	分子重	モノアミンの 種類	モノアミンの 割合 (%)	モノアミンの 割合 (%)
実施例1	15万	APPS/DMC/17	10	80/20
実施例2	15万	APPS/DMC/8F M	40	67/33
実施例3	15万	APPS/DMC/8F	10	68/32
実施例4	15万	MAA/DM/17TN	50	20/80
実施例5	15万	MAA/DM/8F	30	28/74
実施例6	15万	APPS/MA/TAC	53	30/70
実施例7	15万	MAA/DM/17TN	4	40/60
実施例8	15万	APPS/MA/TAC	2.5	75/25
実施例9	140万	APPS/MA/TAC /8F	1.5	85/15
実施例10	8千	APPS/DMC/17 TN	58	14/86
比較例1	15万	MAA/DMC		2/98
比較例2	15万	APPS/DMC		1/99
比較例3	140万	APPS/DM/37TN	0.5	97/3

【0054】 次に、上記実施例及び比較例で得られた組
 成物を以下の評価方法に従って評価試験を行なった。
 尚、評価方法は以下の通りであり、その結果を表2及び
 表3に示す。

【0057】＜繊維の防汚評価＞繊維物の防汚性を評価するため、高分子濃度が5%のサロソールをタオに染め込ませ、乾燥した後、28のラ一油を染み込ませた。その後、洗滌機で洗浄を行い、ラ一油の付着状態を以下

に判定した。その基準は、以下のようである。

- ◎：全く油汚れなし
- ：ほとんど油汚れなし
- △：少し油汚れあり
- ×：油汚れあり

＜防汚性評価＞繊維物の防汚性を評価するため、高分子濃度が5%のサロソールを用い、ウチリルシメサルミアノ酢酸<タ>イン：0.07質量%、ウチリルシメサルミアノ酢酸<タ>イン：0.17質量%、エタノール：5質量%に高分子濃度が5%のサロソールを染み込ませ、乾燥した後、28のラ一油を染み込ませた。その後、洗滌機で洗浄を行い、ラ一油の付着状態を以下の基準で目標判定した。

- ◎：全くラ一油がついていない
- ：ほとんどラ一油がついていない
- △：わずかに残っている
- ×：かなり残っている

【0058】＜防汚性評価＞繊維物及び比較例で得られた高分子濃度が5%のサロソールを染み込ませ、乾燥した後、60℃のお湯の上に放置し、その防汚性を目標で判定した。

- ◎：全く曇らない
- ：ほとんど曇らない
- △：わずかに曇る
- ×：かなり曇る

【0059】＜防汚性評価＞繊維物及び比較例で得られた高分子濃度が5%のサロソールを用い、ウチリルシメサルミアノ酢酸<タ>イン：0.07質量%、ウチリルシメサルミアノ酢酸<タ>イン：0.17質量%、エタノール：5質量%に高分子濃度が5%のサロソールを染み込ませ、乾燥した後、60℃のお湯の上に放置し、その防汚性を目標で判定した。その基準は、以下のようである。

- ◎：全く曇らない
- ：ほとんど曇らない
- △：わずかに曇る
- ×：かなり曇る

【0060】＜防汚性評価＞繊維物及び比較例で得られた高分子濃度が5%のサロソールを用い、ウチリルシメサルミアノ酢酸<タ>イン：0.07質量%、ウチリルシメサルミアノ酢酸<タ>イン：0.17質量%、エタノール：5質量%に高分子濃度が5%のサロソールを染み込ませ、乾燥した後、60℃のお湯の上に放置し、その防汚性を目標で判定した。その基準は、以下のようである。

- ◎：全く曇らない
- ：ほとんど曇らない
- △：わずかに曇る
- ×：かなり曇る

サツル	防汚性 1	8-8"77"77 の付着残り 1	繊維の防汚 性 1	防汚部面 1
実施例 1	◎	○	◎	○
実施例 2	◎	◎	◎	◎
実施例 3	◎	◎	◎	◎
実施例 4	○	◎	○	◎
実施例 5	◎	◎	◎	◎
実施例 6	○	○	◎	◎
実施例 7	◎	◎	◎	◎
実施例 8	◎	○	○	◎
実施例 9	○	○	○	○
実施例 10	○	○	○	○
比較例 1	×	△	×	×
比較例 2	×	×	×	×
比較例 3	×	×	×	×

【表 3】

サツル	防汚性 2	8-8"77"77 の付着残り 2	繊維の防汚 性 2	防汚部面 2
実施例 1	◎	◎	○	◎
実施例 2	◎	◎	◎	◎
実施例 3	◎	◎	◎	◎
実施例 4	○	○	◎	○
実施例 5	◎	◎	◎	◎
実施例 6	◎	◎	○	○
実施例 7	◎	◎	◎	◎
実施例 8	○	◎	○	○
実施例 9	○	○	○	○
実施例 10	○	○	○	○
比較例 1	×	×	△	×
比較例 2	×	×	×	×
比較例 3	×	×	×	×

【0061】以上、結果から実施例1～10による表面処理剤は、防汚性及び防曇性に優れていることが判る。一方、比較例3においては防汚性及び防曇性が劣ると見られず、たとえ比較例3のようにフッ素系モノマーを使用しなくとも、その添加量が少なければ十分な効果が得られない。また、実施例1～8による表面処理剤は、特に優れていることから、フッ素系モノマー量は2.0～5.5%の範囲内が更に好ましいことが判る。また、高分子共重合体の分子量は数十万オーダーのものが

望ましいことが判る。【0062】次に、実施例1乃至実施例20は、フッ素系モノマー（D）を用いたものである。また、モノマー（A）、及びスルホン基含有二ル共重合体の組成比は質量%で示し、フッ素系モノマーは酸型、塩基性モノマーはニオン型を示すものはニオン型として計算し、4級酸型モノマーは対イオンに塩化物を用いた時の組成比として計算した。

[illegible][illegible]

実施例 15	実施例 14	実施例 13	実施例 12	実施例 11
(5)	(4)	(3)	(2)	(1)
重合体	重合体	重合体	重合体	重合体
水の接触角	20°	20°	15°	14°
サラダ油の接触角	83°	85°	80°	85°
硬表面の防汚性	3	3	3	3
軟表面の防汚性	3	3	3	3
防曇性	3	3	3	3

【表5】

実施例 20	実施例 19	実施例 18	実施例 17	実施例 16
(10)	(9)	(8)	(7)	(6)
重合体	重合体	重合体	重合体	重合体
水の接触角	15°	20°	41°	22°
サラダ油の接触角	80°	87°	76°	86°
硬表面の防汚性	3	3	3	3
軟表面の防汚性	3	3	3	3
防曇性	3	3	3	3

【0073】
 【表6】
 に優れた防汚性及び防曇性を付与することが分かる。しかも、かかる基材面は親水親油性を十分に保持していることが分かる。従って、上記フッ素含有高分子重合体を対象表面に処理せしめることにより、優れた汚れ除去性(防汚性)と防曇性を付与することができ、また親水親

【0075】
 【発明の効果】以上説明したように、本発明に係るフッ素含有表面処理剤は、上記式(1)で表されるフルオロアルキル基を有するフッ素系ニルモノマー(A)が1

〜70質量%の範囲で含まれる重合体を有するの
 て、被処理基材に防汚性及び防曇性を十分に付与すること
 ができる。

【0074】以上、結果、実施例1乃至20は基材面

比較例 5	比較例 4	(12)	74°	25°	28°	1	2	1
重合体	重合体	重合体	重合体	重合体	重合体	重合体	重合体	重合体
水の接触角	25°	25°	25°	25°	25°	25°	25°	25°
サラダ油の接触角	83°	83°	83°	83°	83°	83°	83°	83°
硬表面の防汚性	1	1	1	1	1	1	1	1
軟表面の防汚性	1	1	1	1	1	1	1	1
防曇性	1	1	1	1	1	1	1	1

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